Dynamics of the interaction of ethane with Ir(110)-(1×2)

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Experimentally determined values of the initial adsorption probability of ethane on Ir(110)-(1×2) are presented which probe the dynamics of the interaction. The data were obtained from supersonic molecular beam measurements with an incident kinetic energy E_i ranging between 1.2 and 24 kcal/mol, surface temperatures T_S between 77 and 550 K, and incident angle θ_i between 0° and 45°. Experimentally determined values of the initial trapping probability ζ_0 of ethane into a physically adsorbed state at $T_S = 77$ K as a function of E_i and θ_i and experimentally determined values of the initial probability of dissociative chemisorption S_0 as a function of E_i,θ_i, and T_S are presented. The value of ζ_0 is found to decrease with increasing E_i consistent with the fact that an increasingly larger fraction of the incident kinetic energy must be dissipated in order for the molecule to physically adsorb. The initial trapping probability has a relatively weak dependence on θ_i such that the value of ζ_0 is found empirically to scale as $E_i \cos^{0.5} \theta_i$. Two distinct mechanisms of dissociative chemisorption on the bare surface are revealed. At low E_i a temperature-dependent trapping-mediated chemisorption mechanism dominates, while at relatively high E_i a temperature-independent direct mechanism dominates. For E_i less than 13.4 kcal/mol, the value of S_0 decreases rapidly with increasing T_S, consistent with a trapping-mediated mechanism. For a surface temperature of 154 K, S_0 decreases with increasing E_i for $1.2 \leqslant E_i \leqslant 13.4$ kcal/mol, in a manner similar to that for the molecular trapping probability. The data in the low E_i regime also support quantitatively a kinetic model consistent with a trapping-mediated chemisorption mechanism. The difference in the activation energies for desorption and chemisorption from the physically adsorbed, trapped state $E_d - E_c$ is 2.2 ± 0.2 kcal/mol. In the trapping-mediated chemisorption regime, the value of S_0 is found to be rather insensitive to incident angle, scaling with $E_i \cos^{0.5} \theta_i$ just as for trapping of molecular ethane into a physically adsorbed state. For a normal energy $E_i \cos^2 \theta_i$ greater than 8 kcal/mol, chemisorption via a direct mechanism becomes significant and increases with increasing E_i. Values of S_0 in the direct chemisorption regime scale with normal energy and are independent of T_S over the range from 350 to 1350 K.

I. INTRODUCTION

The dynamics and kinetics of the interaction of a molecule with a solid surface combine to form several of the elementary steps inherent in many industrially important processes. Such processes include microelectronics fabrication and heterogeneous catalysis. The dynamics of the interaction of a particle with a surface are of fundamental interest also, dissociative chemisorption and energy exchange at the interface being among the outstanding problems in the field.

Several studies have appeared recently which have begun to elucidate the relevant dynamics involved in the molecule–surface interaction.[1–14] The picture emerging from the results of these studies regarding dissociative chemisorption is one in which the dissociation occurs via a temperature-independent direct mechanism at high incident kinetic energy and a trapping-mediated chemisorption mechanism at low energy.

In the case of the direct mechanism, dissociation is thought to occur upon impact with the surface provided sufficient energy is available to overcome existing activation barriers. A combination of kinetic energy and vibrational energy is effective in promoting dissociation in some cases such that the initial chemisorption probability increases with increasing kinetic and vibrational energy. The trapping-mediated case is quite different. Here the molecule must *lose* sufficient energy to become trapped in a molecularly bound, adsorbed state after colliding with the surface. The molecule remains in this molecularly bound state until it either desorbs from the surface or reorientates into an appropriate configuration for dissociation to occur. Intuitively, one would expect that the trapping probability ζ_0 of a particle impinging on a bare surface would decrease with increasing kinetic energy E_i, since a greater fraction of the incident energy must be dissipated. Indeed, several experimental studies of the trapping dynamics of rare gases and molecules have shown this to be the case.[15–19] A molecule would be expected to trap more readily than a rare gas atom with the same heat of physical adsorption, since translational energy can be converted to rotational and vibrational energy in the molecular case, in addition to substrate excitations.[20–22] Additionally, there is generally a strong dependence on surface temperature T_S in trapping-mediated chemisorption due to the kinetic competition between desorption and dissociative

chemisorption from the trapped state. How the trapping probability scales with incident angle is less intuitive, although several experimental studies with both rare gases and molecules have shown it to be between normal ($E_i \cos^2 \theta_i$) and total energy scaling.[15–19] Although experimental studies of these phenomena are of great practical and fundamental interest, only recently have relevant dynamical data appeared in the literature.[9–13]

This paper is a presentation and discussion of data concerning the interaction of ethane with the Ir(110)-(1×2) surface employing a molecular beam apparatus. In particular we report the following: (1) measurements of the initial trapping probability of molecular ethane into a physically adsorbed state as a function of incident kinetic energy E_i and angle θ_i; and (2) measurements of the initial dissociative chemisorption probability S_0 of ethane as a function of E_i, θ_i, and surface temperature T_S. In an earlier thermal desorption study,[23] evidence was presented for molecular adsorption of ethane on Ir(110)-(1×2) at 100 K. Subsequent heating causes C–H bond cleavage at 130 K in some of the adsorbed ethane with the remainder desorbing. The activation energy for C–H bond cleavage was estimated to be approximately 6 kcal/mol with respect to the bottom of the well for physical adsorption the depth of which is approximately 8 kcal/mol. In a recent molecular beam study of ethane activation on Ir(110)-(1×2) using a beam reflectivity technique, Steinruck *et al.*[14] concluded that there was no evidence for trapping-mediated dissociative chemisorption for surface temperatures between 300 and 1400 K. However, evidence for trapping-mediated chemisorption was revealed in measurements by the same group for propane and *n*-butane on Ir(110)-(1×2).[9] In the work we report here, we find strong evidence indicating that a trapping-mediated mechanism dominates the dissociative chemisorption of ethane on Ir(110)-(1×2) for surface temperatures between 154 and 250 K and for E_i between 1.2 and 13.4 kcal/mol. As expected for a trapping mediated reaction, the value of S_0 decreases with increasing E_i (up to approximately 13.4 kcal/mol) in a manner similar to that of the probability of trapping into the physically adsorbed state. We find that both the value of ζ_0 and S_0 are relatively insensitive to incident angle, nearly scaling with total energy. At higher kinetic energy we find that a temperature-independent direct mechanism dominates the dissociative chemisorption of ethane on Ir(110)-(1×2) which scales with the normal energy, in agreement with the findings of Steinruck *et al.*[14]

II. EXPERIMENTAL METHODS

Measurements of the adsorption probability in the limit of zero surface coverage have been made using the reflectivity method of King and Wells,[24] employing an apparatus that will be described in detail elsewhere.[25] Briefly, the apparatus consists of a thrice differentially pumped, supersonic molecular beam source, and ultrahigh vacuum scattering chamber. Low-energy electron diffraction optics, Auger electron spectroscopy, and an ion gun are mounted on the scattering chamber for obtaining and verifying surface cleanliness and order. A quadrupole mass spectrometer is also mounted on the scattering chamber for thermal desorption mass spectrometry, reflectivity measurements, and beam time-of-flight measurements. The source chambers contain the nozzle, a high-speed shutter, and a chopper for beam modulation as well as apertures for beam collimation. Both the scattering chamber and the third-beam chamber are pumped by turbomolecular pumps; the other two beam chambers are pumped by diffusion pumps. The single crystalline sample was cut from a boule that was oriented with a Laue diffractometer and then polished using standard techniques. The Ir(110)-(1×2) sample is mounted on a manipulator in the scattering chamber which provides precise alignment of the crystal in the beam. The azimuthal orientation of the sample is such that an [001] vector lying in the plane of the sample surface is ~15° from the axis of rotation of the manipulator (i.e., the polar angle). The crystal is cleaned in vacuum by occasional argon ion bombardment and routine annealing in oxygen. Sharp LEED patterns and negligible contamination as judged by Auger spectroscopy are obtained easily with this procedure. The manipulator is liquid nitrogen cooled, providing rapid cooling of the sample to below 80 K. The sample temperature is determined by a 0.003 in. W/5%Re-W/26%Re thermocouple that is spot-welded to the back of the crystal.

As mentioned above, the data reported here for the initial probability of adsorption were determined by a beam reflectivity method similar to that of King and Wells.[31] With this method the partial pressure of ethane in the scattering chamber is used as a measure of the flux of C_2H_6 molecules that do not adsorb. There is no significant steady-state accumulation of physically adsorbed ethane for any of the experimental conditions reported here in which dissociative chemisorption is studied. Initial adsorption probabilities are determined by a comparison of the initial ethane partial pressure, following the opening of the high-speed shutter, to the ethane partial pressure from the beam scattering from the saturated surface. Beam kinetic energies are varied by a combination of seedings and variation of nozzle temperatures, and are measured by time-of-flight techniques.

III. RESULTS AND DISCUSSION

Figure 1 shows ζ_0 for ethane on a 77 K Ir(110)-(1×2) surface at three different indicent angles as a function of $E_i \cos^{0.5} \theta_i$. At $T_S = 77$ K all molecules that trap on the clean surface will remain physically adsorbed since the desorption temperature at low coverages of ethane on Ir(110)-(1×2) is approximately 135 K.[23] This fact has been verified by also measuring ζ_0 at $T_S = 90$ and 110 K. There is no change in ζ_0 for $77 \leqslant T_S \leqslant 110$ K, although there is a reduction in the saturation coverage with increasing T_S. Previous studies of the trapping of Ar on Pt(111)[17] have shown ζ_0 to be sensitive to background contamination on the surface. Indeed, in the measurements reported here, ζ was observed to increase with coverage until near saturation.[26] The effect of background contaminants on the ζ_0 measurements reported here are insignificant since the base pressure in our scattering chamber is $\sim 1 \times 10^{-10}$ Torr, and the sample can be cooled from ~1620 to 77 K in <90 s. Experimental uncertainties in ζ_0 range from ± 0.020 to ± 0.040 with an average uncertainty for all 23 measurements of ± 0.029.

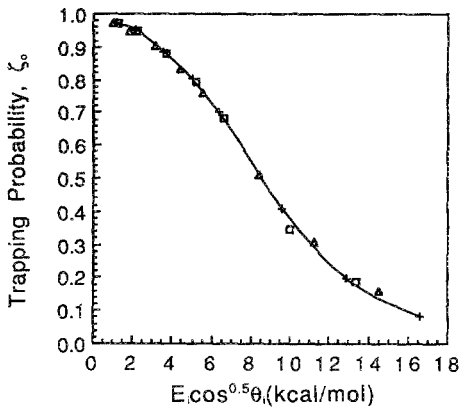

FIG. 1. Trapping probability as a function of $E_i \cos^{0.5} \theta_i$ (kcal/mol) for ethane on Ir(110)-(1×2) at $T_S = 77$ K for θ_i of 0° (□), 22.5° (+), and 45° (△).

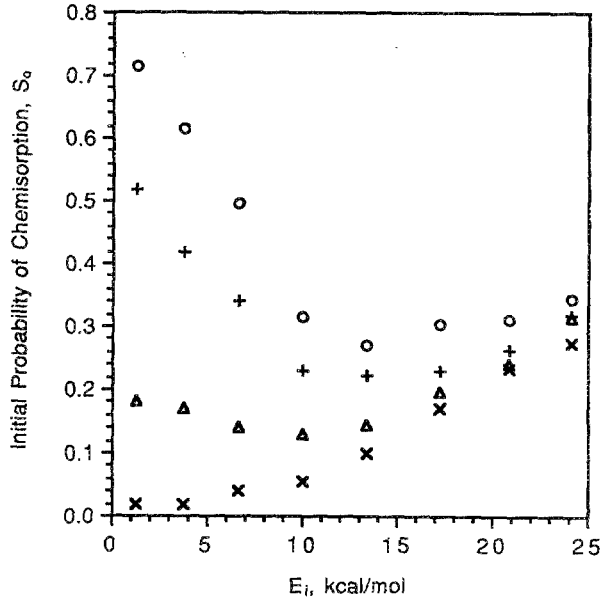

FIG. 2. The initial probability of dissociative chemisorption for ethane on Ir(110)-(1×2) as a function of incident kinetic energy for $T_S = 154$ (○), 182 (+), 250 (△), and 500 (×) K. All measurements shown in this figure were made at normal incidence.

For normal kinetic energies ($E_i \cos^2 \theta_i$) ⩾8 kcal/mol, there is a significant component of direct dissociative chemisorption. Our measured values of the direct chemisorption component have been subtracted from the initial adsorption probabilities for the relevant measurements to obtain values for ζ_0.

The initial trapping probability decreases with increasing E_i since the molecule must dissipate a larger fraction of the normal component of its linear momentum. A simple model illustrates the idea: trapping will occur when the fraction of incident kinetic energy dissipated upon impingement is greater than $E_i/(E_i + \epsilon)$, where ϵ is an effective attractive well depth.[29] We find empirically that the data scale very well with $E_i \cos^{0.5} \theta_i$, as is apparent in Fig. 1. This suggests a rather corrugated interaction potential which is consistent with the corrugated geometrical structure of this reconstructed surface.[27,28]

It is possible that the internal degrees of freedom of the molecule play a role in the dissipation of kinetic energy. Trajectory calculations for NO and N_2 scattering from Ag(111) performed by Tully and co-workers[20–22] demonstrate that conversion of translational to rotational energy during impact makes a very important contribution to trapping for these systems. Additionally, Tully and Cardillo[20] suggest that molecules with low-frequency vibrations can be expected to transfer vibrational energy easily to and from rotational, translational and surface vibrational motion.

Figure 2 shows the initial probability of dissociative chemisorption of ethane on the Ir(110)-(1×2) surface as a function of incident kinetic energy, parametric in surface temperature at normal incidence. For a given surface temperature ($T_S \leqslant 250$ K), S_0 decreases initially as E_i increases, which is consistent with trapping-mediated chemisorption and completely different from that which is expected for direct chemisorption. Indeed the shape of the $S_0(E_i)$ curve for $T_S = 154$ K and $E_i \leqslant 10$ kcal/mol, is very similar to that for the trapping of molecular ethane into a physically adsorbed state on Ir(110)-(1×2) at 77 K, as shown by comparison with Fig. 1. Also apparent in Fig. 2 is the strong dependence of S_0 on T_S, especially at relatively low incident kinetic energies. For E_i greater than approximately 13.4 kcal/mol, S_0 increases with increasing E_i, and there is a significantly weaker dependence on surface temperature. In this higher energy regime, the primary (but not exclusive) mechanism for dissociative chemisorption is the direct mechanism.

As may be seen in Fig. 2, the value of S_0 is a function of T_S at each value of the impact energy. The functional dependence is stronger at lower impact energies since this is the regime in which the trapping-mediated channel of chemisorption is dominant. Trapping-mediated dissociative chemisorption can either be temperature independent, increase with T_S, or decrease with T_S depending on the details of the potential energy surface. A simple model serves to explain the temperature dependence of the trapping-mediated chemisorption of ethane on Ir(110)-(1×2). A gas-phase molecule which impinges on the clean surface traps with a probability of ζ_0 (as displayed in Fig. 1). Once the ethane molecule is trapped in the physically adsorbed state it loses all "memory" of its prior gas-phase conditions and accommodates fully to the surface temperature. A particle in this weakly bound trapped state will eventually either desorb or chemisorb. Here we are concerned with chemisorption in the zero coverage limit, and there is negligible accumulation of physically adsorbed ethane at the surface temperatures at which measurements were carried out. Thus, the rates of chemisorption and desorption from the trapped molecular state are extremely rapid compared to the ethane impingement rate. In this case the probability of dissociative chemisorption for the trapping-mediated component in the zero-coverage limit can then be written as

$$S_0 = \zeta_0 k_c/(k_c + k_d). \quad (1)$$

In the model k_d is the rate coefficient of desorption and k_c the rate coefficient of dissociative chemisorption from the physically adsorbed state. Equation (1) may be rewritten as

$$S_0 = \zeta_0(E_i,\theta_i,T_S)/\{1 + (k_d^{(0)}/k_c^{(0)}) \times \exp[(E_c - E_d)/k_B T_S]\}, \quad (2)$$

where $k_d^{(0)}$ and $k_c^{(0)}$ are the preexponential factors of the two rate coefficients and E_d and E_c are the corresponding activation energies. In Eq. (2) the trapping probability is written explicitly as a function of E_i,θ_i, and T_S. However, we assume surface temperature independence here. A study by Rettner *et al.*[30] of N_2 trapping on W(100) indicates that changing T_S from 300 to 1000 K decreases ζ_0 by less than 20%. Moreover, a recent study of Ar trapping on Pt(111)[17] also indicates that the value of ζ_0 is a relatively weak function of T_S.

A verification of this simple kinetic model would be provided if a plot of $\ln[(\zeta_0/S_0) - 1]$ as a function of $1/T_S$ were linear. For such a case the slope of the line would be equal to $(E_c - E_d)/k_B$, the difference in the activation energies for dissociative chemisorption and desorption from the physically adsorbed well divided by the Boltzmann constant. Figure 3 is such a plot of data for *several* values of E_i and θ_i, for which the measured values of ζ_0 (from Fig. 1) are used in evaluating the ordinate. It is clear that a straight line provides a good fit to all of the data over an extremely wide range of measurements (the ordinate spans a factor of more than two orders of magnitude and the abscissa a ΔT_S of 350 K), providing strong support for the proposed trapping-mediated chemisorption model. The slope of this line corresponds to a value for $E_d - E_c$ of 2.2 ± 0.2 kcal/mol.[31] Since the depth of the physical adsorption well for ethane is approximately 8.0 kcal/mol, the activation barrier to reaction from the physically adsorbed state is approximately 5.8 kcal/mol, in excellent agreement with the earlier study by Wittrig *et al.*[23] The value of the ratio of preexponential factors is equal to $k_d^{(0)}/k_c^{(0)} \sim 390 \pm 100$.[31] A ratio of $k_d^{(0)}/k_c^{(0)}$ that is greater than unity is expected since, entropically, desorption is favored over dissociation due to the limited phase space in which dissociation can occur compared to desorption.

Figure 4 shows the initial probability of dissociative chemisorption of ethane on the Ir(110)-(1×2) surface at $T_S = 550$ K as a function of the normal energy $E_i \cos^2\theta_i$. With a surface temperature of 550 K, the component of dissociative chemisorption due to the trapping-mediated mechanism is too small to measure with the beam reflectivity method employed for this study. Additionally, we find that the value of S_0 is independent of T_S over the range of 350 to 1350 K within our measurement uncertainty ($\leqslant 0.03$), in good agreement with an earlier study of ethane chemisorption on Ir(110)-(1×2) by Steinruck *et al.*[14] Thus, Fig. 4 is a display of the value of S_0 for chemisorption by a direct mechanism. As mentioned earlier a measurable value for chemisorption via the direct mechanism occurs for normal energies greater than or equal to 8 kcal/mol as shown in Fig. 4. It can also be seen that the value of S_0 increases with increasing E_i and is a strong function of θ_i. Indeed the value of S_0 scales quite well with $E_i \cos^2\theta_i$, as shown in Fig. 4 and in agreement with the earlier study by Steinruck *et al.*[14] Normal-energy scaling is quite common for direct, dissociative chemisorption in activated systems,[2,3] however the direct dissociative chemisorption of N_2 on W(110)[1] has been found to scale with total energy. An intriguing aspect of this study is the $E_i \cos^{0.5}\theta_i$ scaling of the value of ζ_0 and S_0 in the trapping-mediated regime versus the $E_i \cos^2\theta_i$ scaling of the direct component of chemisorption. We note that in a study of the chemisorption of N_2 on W(100) Rettner *et al.*[12] found that both the trapping-mediated and the direct components scaled with total energy.

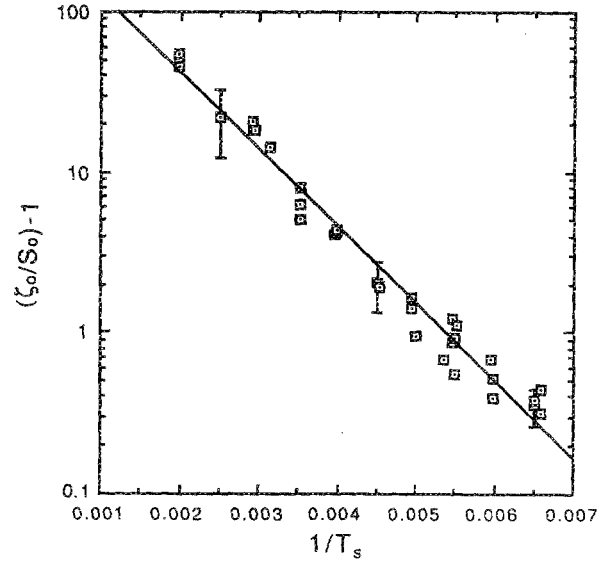

FIG. 3. A plot of $[(\zeta_0/S_0) - 1]$ as a function of $1/T_S$ for several incident kinetic energies and angles. Only the trapping-mediated component of S_0 is used for the ordinate (i.e., the measured direct component of dissociative chemisorption is subtracted from the measured value of S_0).

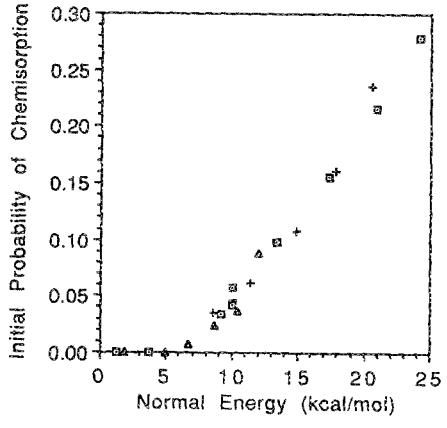

FIG. 4. The initial probability of dissociative chemisorption for ethane on Ir(110)-(1×2) with $T_S = 550$ K as a function of the normal energy ($E_i \cos^2\theta_i$). 0° (□), 22.5° (+), and 45° (△).

IV. SUMMARY

Results from a molecular beam study of the initial probability of adsorption of ethane on an Ir(110)-(1×2) surface have been presented. At $T_S = 77$ K ethane traps into a physically adsorbed state with the trapping probability ζ_0 scaling with $E_i \cos^{0.5} \theta_i$. The physically adsorbed state is a precursor to chemisorption in a mechanism for dissociation which is trapping-mediated. At low E_i the data have many of the characteristics inherent to a trapping-mediated chemisorption channel including (1) the value of the dissociative chemisorption probability S_0 decreases with increasing kinetic energy in a manner similar to that of the value of ζ_0, (2) the data have a strong temperature dependence at low E_i, and (3) the value of S_0 scales as $E_i \cos^{0.5} \theta_i$ just as in the case of trapping into the physically adsorbed state. Moreover, the data in the trapping-mediated chemisorption regime quantitatively fit a kinetic model describing this mechanism. At relatively high kinetic energy, the dominant channel of dissociative chemisorption is a temperature independent direct mechanism. In the direct regime the value of S_0 scales with the normal energy $E_i \cos^2 \theta_i$.

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